Clofibric acid degradation by catalytic ozonation using hydrotalcite-derived catalysts

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ABSTRACT

The degradation of an aqueous solution of clofibric acid was investigated during catalytic ozonation. Mg/Al hydrotalcite (HT) catalysts containing Fe, Cu, and Ni, and spinel-type materials $CuAl_2O_4$ and $CuMgAl_2O_4$ were prepared by co-precipitation method, calcined and used for the ozonation reaction of clofibric acid. The combination of ozone and HT catalysts was effective for the removal of total organic carbon (TOC). MgCuAl HT and $CuMgAl_2O_4$ showed the highest activity, followed by MgFeAl and MgNiAl. The best result of clofibric acid mineralization concerning activity and stability was observed over $Mg_3Fe_{0.5}Al_1$ HT catalyst calcined at 900 °C with no leaching of Fe, and $Cu_{0.75}Mg_{0.5}Al_2O_4$ catalyst after pretreatment with 2% of oxalic acid calcined at 950 °C, with which least leaching of Cu metal was detected. With these materials, up to 70 and 80% of mineralization degree, respectively, was achieved. These materials have shown to be stable after reuse. Also XRD analyses of used catalysts showed similar crystallographic structures than fresh materials. The efficiency of the process is mainly attained by a heterogeneous radical based mechanism, and not significantly affected by initial pH of solution.

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1. Introduction

The presence of environmental xenobiotics such as pharmaceuticals and personal care products in surface and groundwater has become a major cause of concern due to their effects on aquatic life and potential impact on human health. Some of these compounds such as clofibric acid (CFA, a blood lipid regulator) have shown high persistency when they are introduced in the water [1–3]. Clofibric acid is the primary metabolite of clofibrate, a drug used as a lipid regulator which remains in the environment for a long time [4]. Due to its polar character, clofibric acid does not significantly adsorb in soil and can easily spread in surface and groundwater. Its biological effects are not completely understood, but it has been associated with endocrine disruption through interference with cholesterol synthesis [5]. 1.6 ng/L of CFA in the effluent of a German treatment plant, 270 ng/L in drinking water samples from the Berlin area, various ng/L in drinking water in Lombardy, Italy, and 1 ng/L in different samples taken in the North Sea were reported by several authors [6–10]. The conventional techniques like sand filtration and coagulation may not operate with an appropriate efficiency to eliminate such compounds, in particular for the drinking water treatment [11]. One way to reduce these contaminants is to decrease their presence by the "on-site" treatment of pharmaceutical plant wastewaters. Advanced oxidation processes (AOP) have been found to be effective in the removal of these compounds even in low concentrations. Ozone, a powerful oxidizing agent, is effective for the mineralization of refractory organic compounds. However, in many cases is not able to achieve a complete oxidation of organic compounds. One of the alternatives in order to have greater mineralization efficiency is to promote the process via the generation of free hydroxyl radicals, which are more powerful than molecular ozone, by means of homogeneous or heterogeneous catalysis [12–14]. The activity of a heterogeneous catalyst in ozonation depends on its ability to adsorb ozone. The adsorption of ozone on the surface is a key factor, because it can be followed by the ozone decomposition to hydroxyl radicals. The decomposition of ozone can take place on different types of active centers, and basicity and acidity of surface plays an important role in the process. The transition metals Co, Fe, Ni, Zn and Cu have been widely studied in the form of single or supported metal oxide. Cu as CuO was used as a catalyst for ozonation of different types of organic pollutants such as herbicides (e.g. alachlor), chlorophenols, nitrophenols and carboxylic acid (oxalic acid). It was found to improve TOC removal by promotion of hydroxyl radical formation through the ozone decomposition [15–17].

Hydrotalcites have been used as catalysts since they contain various transition metal cations as the catalytically active species well dispersed on the basic support materials and the oxides obtained by calcination possess interesting properties such as high surface area and basic properties.

It has been reported that the incorporation of Cu into the hydrotalcite structure followed by calcination at 600 °C leaded to a

catalyst with least metal leaching during catalytic ozonation of phenol and oxalic acid [18]. Enhanced dispersion of Cu atoms through the hydrotalcite matrix can be a reason of such a high activity. Also, Co as CoNiAl-hydrotalcite showed higher activity in catalytic ozonation of phenol with respect to CoO, Co_3O_4 and Co supported on CeO_2 and Al_2O_3 [19,20].

In this work we have focused our attention on the use of different types of hydrotalcite-derived materials as heterogeneous catalysts combined with ozone for carrying out the mineralization of clofibric acid solutions. Catalysts containing Fe, Cu and Ni were prepared starting from Mg/Al hydrotalcite and activity and stability of catalysts derived from hydrotalcite-like materials have been studied in the ozonation of CFA. Spinel-type materials $CuAl_2O_4$ and $CuMgAl_2O_4$ were also synthesized via co-precipitation with different molar ratios and were characterized using different techniques. The effect of metal leaching on the ozonation process was studied. The performance of this process was evaluated by the measurement of CFA concentration and total organic carbon (TOC). Also, tests with a lower range of CFA concentration (closer to values that may be found in pharmaceutical plant wastewaters) have been performed to assess the suitability of these catalysts at this range.

2. Experimental

2.1. Catalyst preparation

Mg/Al hydrotalcites (HT) precursor was obtained according to the standard co-precipitation method. Appropriate amounts of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (supplied by Sigma–Aldrich, 99% purity) were dissolved in distilled water and added dropwise into a vessel containing deionized water. The pH was maintained at 10 by simultaneous addition of a 2 M NaOH solution. Both solutions were mixed under vigorous stirring and kept for aging at 60 °C for 24 h. The precipitated solid was filtered and washed several times with de-ionized water and dried at 100 °C to yield the (as-)synthesized hydrotalcite and finally calcined in a muffle furnace in a static air atmosphere at various temperatures (450 °C, 600 °C, 900 °C, 950 °C) for 6 h to obtain the corresponding mixed oxides (calc). $Mg_3Fe_{0.5}Al_1$, $Mg_3Cu_{0.5}Al_1$ and $Mg_3Ni_{0.5}Al_1$ hydrotalcite and $CuAl_2O_4$ and $CuMgAl_2O_4$ spinel-type materials were also prepared by the same method adding the appropriate amounts of $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ with $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (supplied by Sigma–Aldrich, 99% purity). The powders of the mixed oxide, thus obtained, were used as catalysts.

Fe, Cu and Ni metals supported on alumina were prepared for comparison by impregnation method using the same amount of metal that was present in the corresponding calcined hydrotalcites at 450 °C for 6 h.

2.2. Catalysts characterization

Metal content of the hydrotalcite samples was measured by ICP-OES (SPECTRO-ARCOS FHS16). The structure of the catalysts was studied by XRD and N_2 physisorption method. XRD measurements were made using a Bruker-AXS D8-Discover diffractometer with parallel incident beam (Göbel mirror) and vertical theta–theta goniometer, XYZ motorized stage mounted on an Eulerian cradle, diffracted-beam Soller slits, a 0.02° receiving slit and a scintillation counter as a detector. The angular 2θ diffraction range was between 5 and 70°. The data were collected with an angular step of 0.05° at 3 s per step and sample rotation. Cu_k radiation was obtained from a copper X-ray tube operated at 40 kV and 40 mA ($\lambda = 1.541$ Å). N_2 adsorption was performed using a Micromeritics ASAP 2010 apparatus at 77 K. Before analysis, the samples were degassed at 120 °C

for 12 h. Total surface area was calculated by the BET method. The point of zero charge pH_{PZC} of the catalyst was measured by the so-called pH drift method [21].

2.3. Experimental procedure

The ozonation reactions were performed in a 1.5 L glass reactor containing a 500 mL aqueous solution of CFA (100 mg/L or 25 mg/L) at ambient conditions (25 ± 2 °C) and atmospheric pressure. Higher concentrations than those commonly found in wastewaters were used to compare the efficiency of the different catalysts tested and to favor the accuracy in the analytical determinations. To the CFA solution, 250 mg catalyst was added and the ozone generated by an ozone generator (ANSEROS COM-AD-02) from pure O_2 (40 L/h) was passed through the solution maintaining a constant production of 1.2 g/h of O_3. The samples were taken at regular time intervals and quenched using $Na_2S_2O_3$. CFA concentrations were measured by high performance liquid chromatography HPLC (Shimadzu LC-2010 equipped with a SPD-M10A Diode array UV–vis detector) at wavelength 254 and 230 nm. A Varian OmniSpher C18 column and a solution containing an aqueous buffer (Milli-Q H_2O 1 L, methanol 50 mL and H_3PO_4 4 mL) and acetonitrile (40:60) was used as mobile phase. TOC was measured by a Shimadzu 5000-A TOC analyzer.

3. Results and discussion

3.1. Catalysts characterization

Metal content analysis of the samples shown in Table 1S (see Supporting Information), indicates that experimental Mg/Fe/Al, Mg/Cu/Al and Mg/Ni/Al (as-synthesized and calcined) weight ratios are similar to the theoretical values. Co-precipitation for the hydrotalcite samples was carried out effectively. Calcination of the sample up to 450 °C caused the removal of NO_x, CO_2 and H_2O. XRD patterns and N_2-physisorption analysis results of the as-synthesized and calcined catalysts are shown in Table 1.

All calcined hydrotalcite catalysts show higher surface area compared to the synthesized ones except $Ni_2Cu_1Al_1$. After calcination at 450 °C, periclase phase appears which increases the surface area. Synthesized hydrotalcite $Ni_2Cu_1Al_1$ and calcined $Cu_3Ni_{0.5}Al_l$ show the highest surface area up to 127 m^2/g and 121 m^2/g, respectively.

A higher surface area was observed for the spinel-type catalysts prepared by co-precipitation method. Surface area decreases with increase in calcination temperature suggesting that porous structure originated from the initial structure collapses and the crystallization of spinel phase progress. Hence all calcined spinel type materials show very low surface area. Among all the above catalysts, $Cu_{0.25}Mg_{0.75}Al_2O_4$ possesses the highest surface area (161.5 m^2/g) and $Cu_{0.75}Mg_{0.25}Al_2O_4$ the lowest one (15.6 m^2/g).

Crystalline phases of the as-synthesized and calcined catalysts are summarized in Table 1. The as-synthesized hydrotalcites clearly show hydrotalcite crystal phase with small amount of tenorite in the case of Cu hydrotalcite. It is also well-known that Cu-HT is always mixed with other phases such as tenorite, malachite, or gerhardtite, due to the Jahn–Teller effect at the Cu^{2+} ion [22,23]. As it is seen in Table 1, in the Cu-HT samples the presence of tenorite has been confirmed. When these materials were calcined at 450 °C, disappearance of the HT phase with formation of metal oxide phase occurred and hence in this case periclase and bunsenite (in Ni-hydrotalcite) and tenorite crystal phases were detected.

In all spinel-type as-synthesized catalysts, tenorite and bayerite were detected as main phases. With increasing calcination temperature at 900 °C, the spinel ($MgAl_2O_4$ or $CuAl_2O_4$) phase appeared together with small amount of tenorite and corundum crystal

Table 1
Crystalline phases and BET surface area of the synthesized and calcined catalysts.

Catalyst	Synthesized		Calcined	
	Crystal phase[c]	BET surface area (m^2/g)	Crystal phase[c]	BET surface area (m^2/g)
$Mg_3Fe_{0.5}Al_1$ [a]	HT	92.8	Periclase, hercynite	94.2
$Mg_3Cu_{0.5}Al_1$ [a]	HT	98.3	Tenorite, periclase	102.0
$Mg_3Ni_{0.5}Al_1$ [a]	HT	105.0	Periclase, bunsenite	116.0
$Cu_3Ni_{0.5}Al_1$ [a]	HT, tenorite, bayerite	107.0	Bunsenite, tenorite	127.0
$Ni_2Cu_1Al_1$ [a]	HT	121.0	Bunsenite	119.0
$Cu_1Al_2O_4$ [b]	Tenorite, bayerite	121.3	Spinel, tenorite	23.2
$Cu_{0.75}Mg_{0.25}Al_2O_4$ [b]	Tenorite, bayerite	94.2	Spinel, tenorite, corundum	15.6
$Cu_{0.5}Mg_{0.5}Al_2O_4$ [b]	Tenorite, bayerite	123.2	Spinel, tenorite	19.5
$Cu_{0.25}Mg_{0.75}Al_2O_4$ [b]	Bayerite	161.5	Spinel	34.1

[a] Calcination temperature = 450 °C.
[b] Calcination temperature = 900 °C.
[c] HT, hydrotalcite; periclase, MgO; tenorite, CuO; bayerite, $Al(OH)_3$; bunsenite, NiO; spinel, $MgAl_2O_4$ or $CuAl_2O_4$; corundum, Al_2O_3; hercynite, $Fe^{2+}Al_2O_4$.

phases. Pure single spinel phase was observed in calcined $Cu_{0.25}Mg_{0.75}Al_2O_4$ catalyst.

The pH of solution plays an important role in understanding the mechanism of ozonation processes, since it affects ozone decomposition but also because of the different reactivity that present the molecular and ionic form of compounds in front of ozone. Furthermore it determines surface properties of catalyst and properties of analysts being oxidized. Therefore, the pH_{PZC} of $Mg_3Fe_{0.5}Al_1$ (calcined at 900 °C) and $Cu_{0.75}Mg_{0.25}Al_2O_4$ (treated with 2% oxalic acid and calcined at 950 °C) was measured using the pH drift method [21], as shown in Fig. 1S (see Supporting Information). The pH_{PZC} values for the $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ catalysts are 8.2 and 8.4, respectively. These catalysts present basic character according to the pH_{PZC} measurement results. The reactions in the presence of these catalysts have been performed at pH < pH_{PZC} but also at pH > pH_{PZC} and pH = pH_{PZC}.

3.2. Catalytic ozonation of clofibric acid

The results of CFA degradation after 2 h and 6 h by catalytic ozonation using different HT catalysts have been summarized in Table 2.

The reaction using single ozonation resulted in a fast disappearance of CFA in less than 15 min. However the ability of the system in TOC removal was not higher than 28% and 40% after 2 h and 6 h, respectively. Degradation of clofibric acid by ozonation in presence of different hydrotalcite catalysts was tested and similar to single ozonation, CFA conversion was completed in less than 15 min in all cases. Synthesized and calcined MgAl hydrotalcite show 60% and 55% TOC removal after 6 h of reaction. Using MgFeAl hydrotalcite, a clear promotion of the efficiency of the system was observed due to higher TOC removal (66% in 2 h and 78% after 6 h of reaction) with respect to single ozonation. It can be seen that the efficiency in mineralization was greatly enhanced by the addition of HT-derived catalysts when compared to single ozonation. The Fe, Cu and Ni hydrotalcite calcined at 450 °C show 71, 77 and 65% of mineralization in 6 h, respectively. The as-synthesized and calcined at 450 °C $Cu_3Ni_{0.5}Al_1$ hydrotalcite achieved 89% of TOC removal after 6 h. Nevertheless, a high leaching of Cu was observed (4.8 and 6.5 mg/l (see Table 3) for as-synthesized and calcined catalysts, respectively).

When using the as-synthesized and calcined Fe-HTs, no leaching of Fe was observed (see Table 3). However, a large leaching of Mg (28.9 mg/L for as-synthesized and 32.7 mg/L for calcined HT) was observed after 6 h. Using Cu-based hydrotalcite leads to further improvement in the results, particularly concerning TOC removal (89% for synthesized $Cu_3Ni_{0.5}Al_1$ and 91% for calcined $Ni_2Cu_1Al_1$) but for both catalysts a high leaching of Cu (4.6 mg/L) and Ni

Table 2
CFA degradation results using single O_3 and catalytic ozonation with HTs-based catalysts.

Catalysts	TOC removal (%)	
	2 h	6 h
Single ozonation	28.0	40.0
Mg_2Al_1 [a]	53.0	60.0
Mg_2Al_1 [b]	45.6	55.2
$Mg_3Fe_{0.5}Al_1$ [a]	66.5	78.3
$Mg_3Fe_{0.5}Al_1$ [b]	60.0	71.1
$Mg_3Fe_{0.5}Al_1$ [c]	57.5	70.8
$Mg_3Fe_{0.5}Al_1$ [d]	52.7	62.0
$Mg_3Cu_{0.5}Al_1$ [a]	74.1	82.2
$Mg_3Cu_{0.5}Al_1$ [b]	65.7	77.2
$Mg_3Cu_{0.5}Al_1$ [c]	60.0	72.0
$Mg_3Ni_{0.5}Al_1$ [a]	46.1	69.8
$Mg_3Ni_{0.5}Al_1$ [b]	65.7	65.3
$Cu_3Ni_{0.5}Al_1$ [a]	79.9	89.6
$Cu_3Ni_{0.5}Al_1$ [b]	79.0	89.2
$Cu_3Ni_{0.5}Al_1$ [c]	36.4	70.2
$Ni_2Cu_1Al_1$ [a]	70.4	83.9
$Ni_2Cu_1Al_1$ [b]	80.0	90.7
$Ni_2Cu_1Al_1$ [c]	42.0	59.0

[a] As-synthesized.
[b] Calcination temperature = 450 °C.
[c] Calcination temperature = 900 °C.
[d] Calcination temperature = 600 °C.

Table 3
Metal leached to solution during the ozonation test.

Catalyst	Metal leaching (mg/L)							
	2 h				6 h			
	Mg	Cu	Ni	Fe	Mg	Cu	Ni	Fe
Mg_2Al_1 [a]	9.2				17.9			
Mg_2Al_1 [b]	7.7				13.7			
$Mg_3Fe_{0.5}Al_1$ [a]	16.5			0	28.9			0
$Mg_3Fe_{0.5}Al_1$ [b]	16.1			0	32.7			0
$Mg_3Fe_{0.5}Al_1$ [c]	2.1			0	2.8			0
$Mg_3Fe_{0.5}Al_1$ [d]	5.8			0	8.7			0
$Mg_3Cu_{0.5}Al_1$ [a]	7.4	2.1			13.5	2.8		
$Mg_3Cu_{0.5}Al_1$ [b]	32.2	1.8			42.6	2.6		
$Mg_3Cu_{0.5}Al_1$ [c]	5.1	2.1			4.6	1.7		
$Mg_3Ni_{0.5}Al_1$ [a]	15.1		4.5		23.1		5.3	
$Mg_3Ni_{0.5}Al_1$ [b]	15.1		2.3		19.8		3.7	
$Cu_3Ni_{0.5}Al_1$ [a]		2.9	1.8			4.8	2.4	
$Cu_3Ni_{0.5}Al_1$ [b]		1.9	1.2			6.5	1.2	
$Cu_3Ni_{0.5}Al_1$ [c]		2.6	0			3.8	0	
$Ni_2Cu_1Al_1$ [a]		2.2	1.4			2.9	2.6	
$Ni_2Cu_1Al_1$ [b]		1.5	3.9			4.6	4.0	
$Ni_2Cu_1Al_1$ [c]		0	1.1			0	0	

[a] As-synthesized.
[b] Calcination temperature = 450 °C.
[c] Calcination temperature = 900 °C.
[d] Calcination temperature = 600 °C.

(4.0 mg/L) was observed after 6 h of ozonation. The ozonation test using $Mg_3Cu_{0.5}Al_1$ (synthesized and calcined) hydrotalcite shows high TOC removal (82% and 77%, respectively) but a high leaching of Mg (42.6 mg/L) was also observed.

To improve the stability of Fe, Cu and Ni based hdyrotalcites, they were calcined at higher temperature (900 °C) and tested in the catalytic ozonation of CFA. In this case it was observed that there was lower leaching of Mg and Cu as compared to 450 °C of calcination temperature. However, and on the contrary of work by Shiraga et al. [18] did not improve the mineralization efficiency.

At the view of the results, it can be seen that Cu and Ni containing HTs show better performance in catalytic ozonation but present less stability. Fe containing HT was more stable, with good activity in catalytic ozonation of CFA. Among all tested HT-catalysts, $Mg_3Fe_{0.5}Al_1$ calcined at 900 °C is the one that presents the best degree of mineralization with the lowest leaching of Mg metal. All catalysts were tested for adsorption, showing negligible adsorption of CFA.

For comparison, 8.7 wt% of Fe, 12.8 wt% of Cu and 3.5 wt% of Ni were also supported on alumina by impregnation method using the same amount of metal that was present in the corresponding hydrotalcite. Alumina-supporting metal catalysts together with reference materials MgO and Al_2O_3, were tested in ozonation reaction for 2 h, as shown in Table 2S (see Supporting Information). These types of materials show 15–25% of improvement when compared to single ozonation reaction; however a large metal leaching in case of Cu and Ni catalysts is observed. Hence it can be seen that metals incorporated in the structure of a HT and further calcined show better activity in catalytic ozonation of CFA than simply impregnated on an alumina support. The higher activities of these materials are probably due to the stable and highly dispersed active metals species obtained in the HT support after calcinations [14].

3.3. Contribution of homogeneous mechanism due to leached metal

In all the tested catalysts it was observed that when calcined at higher temperature, leaching of metals decreases but also TOC removal does.

In order to evidence the effect of dissolved Mg^{2+}, Ni^{2+}, Al^{3+} and Cu^{2+} on the performance of CFA degradation by ozone, homogeneous catalytic ozonation experiments were performed using dissolved Mg^{2+}, Ni^{2+}, Al^{3+} and Cu^{2+} with a concentration in the range of the maximum leached value found, i.e. 43, 5, 3 and 3 mg/L, respectively. The results of these experiments are shown in Fig. 2S (see Supporting Information), indicating a slight improvement with respect to single ozonation. Complete degradation of CFA was also observed within 15 min.

In the presence of 43 mg/L Mg^{2+}, TOC removal increased by 15% as compared to single ozonation. In homogeneous tests with 5 mg/L Ni and 3 mg/L Cu, TOC removal increased by a 10%. This means that dissolved metals can moderately enhance the ozonation process.

3.4. Improvement of stability

In order to improve the stability of the Cu catalysts, spinel-type materials such as $CuAl_2O_4$ and $CuMgAl_2O_4$ with different molar ratios were prepared and calcined at 900 °C to obtain pure spinel phase (as shown in Table 1). The stability and activity of this type of materials in the catalytic ozonation of CFA was tested.

The results of CFA degradation in 6 h by catalytic ozonation using different HT-derived spinel catalysts have been summarized in Fig. 1.

The fast disappearance of CFA in less than 15 min was observed, as with HTs catalysts. However, a higher efficiency in TOC removal
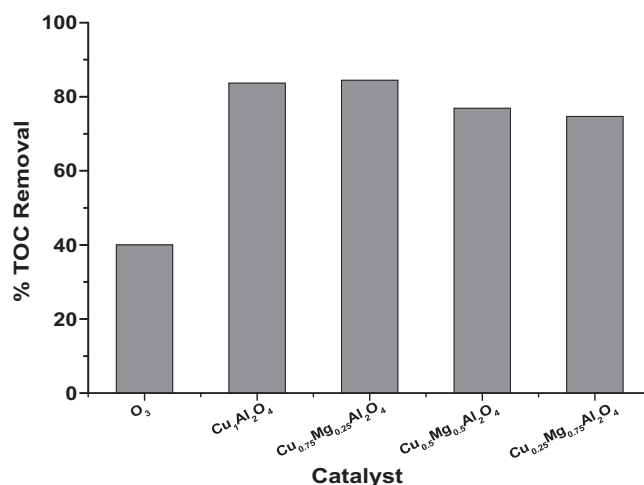

Fig. 1. Mineralization degrees achieved after 6 h treatment with spinel-type catalysts.

(up to 70–85%) was observed using these materials with respect to single ozonation.

From Fig. 3S (see Supporting Information) and Table 1 it can be seen that all these materials show spinel phase with high intensity and tenorite crystal phase with lower intensity. Concerning stability of the catalysts, from Table 4 it can be observed that leaching of Cu and especially Mg considerably decreased when compared to Cu hydrotalcite (see Table 3).

Therefore, and by obtaining of the spinel phase, there is a great improvement in the stability of these materials with respect to Mg (which has shown a remarkable effect in homogenous catalytic tests), while presenting a high activity in the mineralization of CFA.

Best results have been obtained with $Cu_1Al_2O_4$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ catalysts, showing degrees of mineralization up to 83 and 85%, respectively; however, leaching of Cu was found to be 3.5 and 2.2 mg/L, respectively (see Table 4), which is still high.

3.5. Pre-treatment with oxalic acid to diminish the leaching of metals

As commented above, amount of Cu leached is still too high, and this could involve problems of toxicity in the effluents. One hypothesis is that leached Cu could proceed from Cu phases different from the pure spinel one. As commented previously, the tenorite phase observed in the as-synthesized (due to the Jahn–Teller effect) and calcined samples (due to the partial solubility of the CuO phase in the inorganic matrix) could be responsible for the instability of the catalyst. In order to check this and with the aim to remove the excedent phases, after the calcination of $Cu_{0.75}Mg_{0.25}Al_2O_4$ and $Cu_1Al_2O_4$ at 900 °C a treatment with an aqueous solution of 2% oxalic acid was performed and afterwards again calcined at 950 °C. These materials were tested as well in the catalytic ozonation reaction for 6 h and leaching tests were carried out.

Table 4
Leaching results of spinel-type catalysts after 6 h reaction.

Catalyst	Leached metal (mg/L)	
	Cu	Mg
$Cu_1Al_2O_4$	3.5	–
$Cu_{0.75}Mg_{0.25}Al_2O_4$	2.2	1.6
$Cu_{0.5}Mg_{0.5}Al_2O_4$	2.4	2.5
$Cu_{0.25}Mg_{0.75}Al_2O_4$	2.4	1.2

Table 5
Leaching and TOC removal results of spinel-type catalysts after pre-treatment with 2% oxalic acid.

Catalyst	% TOC removal		Leached metal (mg/L)			
	2 h	6 h	2 h		6 h	
			Cu	Mg	Cu	Mg
$Cu_1Al_2O_4$	53.3	76.0	1.1		1.5	
$Cu_{0.75}Mg_{0.25}Al_2O_4$	54.4	79.0	0.7	0.06	1.3	0.1
Cu^{2+} (1.5 mg/L)	33.9	41.8				

Fig. 3. Mineralization degrees obtained by recycling of catalysts after 6 h treatment. (A) Reused catalyst $Cu_{0.75}Mg_{0.25}Al_2O_4$ (pre-treated with 2% of oxalic acid and calcined at 950 °C) and (B) Reused catalyst $Mg_3Fe_{0.5}Al_1$ (calcined at 900 °C).

From Table 5 it can be observed that leaching of Cu and Mg was minimized (maximum values Cu: 1.5 and Mg: 0.1 mg/L) after the pretreatment with 2% of oxalic acid. Using $Cu_1Al_2O_4$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ catalysts, mineralization degrees of CFA achieved after 6 h treatment were 76 and 79%, respectively.

Again, in order to evidence the effect of dissolved Cu^{2+} on the performance of CFA degradation by ozone, a homogeneous catalytic ozonation experiment was performed using dissolved Cu^{2+} with a concentration of 1.5 mg/L. The result of this experiment is shown in Table 5. Complete degradation of CFA was observed within 15 min. It can be seen that the presence of dissolved Cu^{2+} in this concentration does not effectively enhance the ozonation process with respect to single ozonation (Table 3) after 6 h reaction; therefore this amount of leached Cu does not contribute to the overall percentage of mineralization achieved, which is mostly due to the heterogeneous contribution.

XRD pattern of fresh and used catalysts is shown in Fig. 4S (see Supporting Information). The catalyst structure almost remains the same after the reaction. In the case of used catalysts, a reduction in crystalinity and decrease in peak intensity was observed. Also, in the case of $Mg_3Fe_{0.5}Al_1$ catalyst, a partial recovery of initial hydrotalcite structure is observed in used catalyst, due to the "memory effect" [24]. Among this set of materials, $Mg_3Fe_{0.5}Al_1$ (calcined at 900 °C) hydrotalcite and $Cu_{0.75}Mg_{0.25}Al_2O_4$ (treated with 2% oxalic acid and subsequent calcination at 950 °C) have shown to be the most stable and active catalysts in the catalytic ozonation of CFA.

The evolutions of TOC with these materials along with single ozonation during 6 h reaction are shown in Fig. 2. It reveals that the main TOC reduction for each reaction occurs during the first 2 h of treatment. This means that the degradation of CFA and readily oxidizable intermediates occurs at the same time. The rest of the reaction time was assigned to the degradation of other oxidizable intermediates.
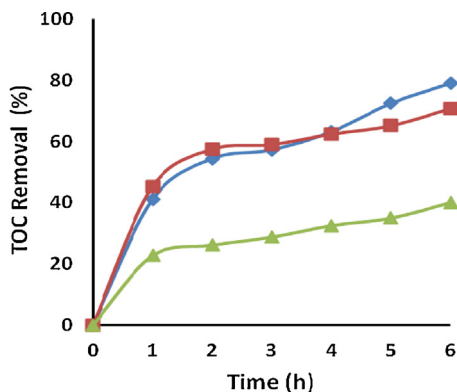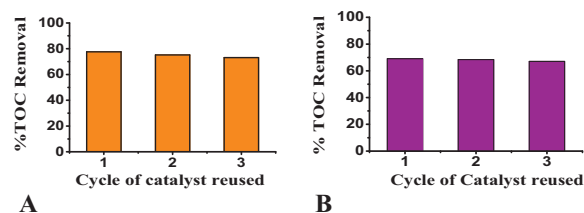
3.6. Reuse and recycling of catalyst

The two catalysts that have shown to be more active and stable were $Cu_{0.75}Mg_{0.25}Al_2O_4$ and $Mg_3Fe_{0.5}Al_1$, achieving mineralization degrees of 55 and 58% after 2 h, and 79 and 70% after 6 h, respectively. To the best of our knowledge, and apart from our previous study of catalytic ozonation of CFA with cupper dawsonites [13], there is only one reference [25] dealing with the catalytic ozonation of CFA, who achieved a %TOC removal after 2 h of treatment of 20 and 40% at pH 3 and 5, respectively. Therefore, these materials are promising catalysts for the catalytic ozonation of CFA and related compounds.

CFA degradation was tested in the presence of $Cu_{0.75}Mg_{0.25}Al_2O_4$ and $Mg_3Fe_{0.5}Al_1$ recovered after a run by filtering, washing and drying, and reused in three consecutive runs to assess its stability, as shown in Fig. 3.

Like in the case of fresh catalysts, a total disappearance of CFA occurred in less than 15 min. It can be seen that catalytic activity of these catalysts was maintained, as they show near about 73% and 67% TOC removal, respectively, when reused in three consecutive cycles for 6 h of ozonation reaction. These results corroborate the improvement in the stability of these materials.

The single ozonation and catalytic ozonation with lower concentration of CFA (25 mg/L) was also studied using these two catalysts, at free pH. In test with single and catalytic ozonation, concentrations below our detection limit (0.1 mg/L) were detected after 7 min reaction. Calcined $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ (2% oxalic acid pre-treatment) show both 58% in 2 h and 73% and 81% TOC removal after 6 h of reaction (see Fig. 4). It can be seen therefore that the efficiency in mineralization was maintained or even slightly enhanced at lower concentration values of CFA.
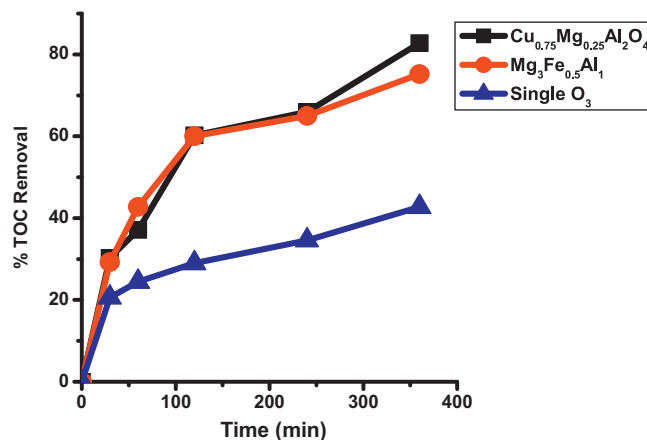

Fig. 2. TOC removal (%) with calcined $Mg_3Fe_{0.5}Al_1$ (-■-) and $Cu_{0.75}Mg_{0.25}Al_2O_4$(2% oxalic acid pre-treatment) (-◆-), and by single ozonation (-▲-).

Fig. 4. TOC removal (%) during the CFA (25 mg/L) degradation by catalytic ozonation using calcined $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$(2% oxalic acid pre-treatment), and by single ozonation.
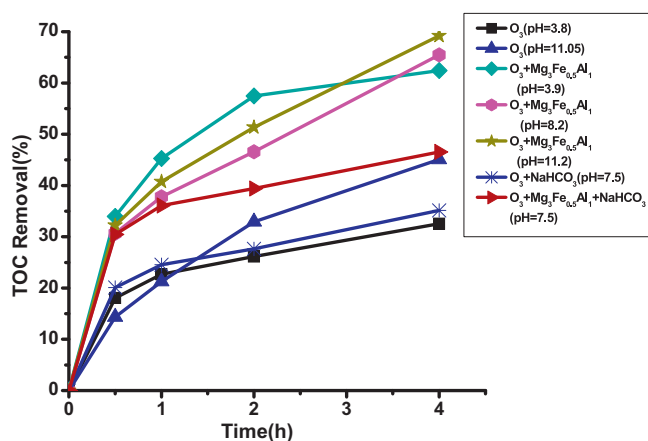
Fig. 5. TOC removal (%) during the CFA degradation by single ozonation and catalytic ozonation (with $Mg_3Fe_{0.5}Al_1$ calc at 900 °C) at different pHs and in presence and absence of $NaHCO_3$.

Fig. 6. TOC removal (%) during the CFA degradation by single ozonation and catalytic ozonation (with $Cu_{0.75}Mg_{0.25}Al_2O_4$ treated with 2% oxalic acid and calcined at 950 °C) at different pHs and in presence and absence of $NaHCO_3$.

3.7. Study of mechanism of the catalytic ozonation process

As it has been seen in previous results, removal of CFA is accomplished in less than 15 min (for an initial CFA concentration of 100 mg/L) in presence or absence of a catalyst. Kinetic rate constant of ozone with clofibric acid has been established by Rosal et al. [25], being $3.5 M^{-1} s^{-1}$ at pH 1 and $14.3 M^{-1} s^{-1}$ at pH 5. The main action of the catalysts is observed in the enhancement of the mineralization degree, i.e. in the degradation of intermediates produced. Although charged surface of the catalyst at initial pH of 4 (below the point of zero charge) might favor the adsorption of ionizable compounds, when these catalysts were tested for adsorption, negligible adsorption of CFA on catalyst surface was observed. Therefore, the contribution of the adsorption of CFA in mineralization is not expected to be important. Furthermore, a possible Langmuir–Hinshelwood mechanism in which reaction takes place with both species (ozone and CFA) adsorbed is rejected.

Rate constant of OH radicals with CFA has also been determined by [25], being $5.5 \times 10^9 M^{-1} s^{-1}$. The role of hydroxyl radicals during the catalytic ozonation was investigated by performing some tests in the presence of a radical scavenger ($NaHCO_3$) that does not interfere in TOC analysis. Like the reaction without radical scavenger, CFA was totally removed in the presence of $NaHCO_3$ in 15 min. However, TOC removal results clearly demonstrate the effect of the radical scavenger, as shown in Figs. 5 and 6. The ozonation using the most stable and active catalysts $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ in the presence of $NaHCO_3$ at free pH (pH of the solution was slightly lower than pH_{PZC}), shows a significant decrease in TOC removal. Also a reaction of single ozonation at pH 11 was performed, leading to some improvement in mineralization (51%) when compared to single ozonation at acidic pH but lower than with the addition of the heterogeneous catalysts.

As in the presence of a radical scavenger the efficiency of the catalysts is significantly hindered, we can conclude that one of the main roles of these materials in the catalytic ozonation of CFA is likely to contribute to the generation of hydroxyl radicals by decomposition of ozone, but the reaction would take place in solution, as the interaction of surface sites and CFA is probably limited. When introduced in water, metal oxides tend to strongly adsorb H_2O molecules, which in turn dissociate into H^+ and OH^-, forming surface hydroxyl groups with the oxygen sites and surface metal, respectively [26]. Surface hydroxyl groups have been found to promote $OH^\bullet$ generation from aqueous ozone [27,28].

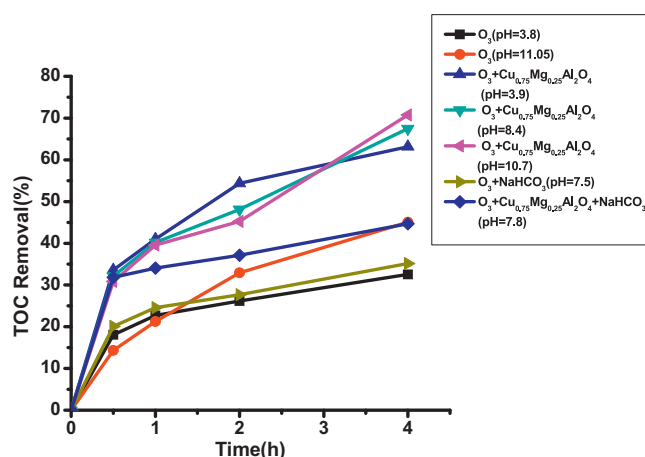In order to study the effect of pH on the performance of CFA degradation by ozonation using these catalysts, the process was carried out at different initial pH (pH = pH_{PZC}, pH < pH_{PZC} and pH > pH_{PZC}), as shown in Figs. 5 and 6. For that, the pH of a 100 mg/L CFA solution was adjusted at initial pH 8.2–8.4 (pH = pH_{PZC}), and 10.7–11.2 (pH > pH_{PZC}) by NaOH. Nevertheless, by starting these reactions, the pH dropped to <5 in 5–10 min, likely due to the formation of large amount of acidic intermediates.

Solutions have not been buffered to avoid the presence of ions that may interfere in the process. E.g. phosphate ions have been found to substitute surface hydroxyl groups [28,29]. As for the form of clofibric acid in solution, its pK_a is 3.2 [22], therefore it dissociates in aqueous solutions even under acidic conditions.

The reaction at pH 8.2 and 11.2 using $Mg_3Fe_{0.5}Al_1$ (see Fig. 5) attained slight improvement of the TOC removal (65% and 69%, respectively) with respect to the reactions at lower pH 4 (62%). TOC profile of this reaction shows a slower TOC elimination during the first 2 h as compared to the reaction at pH 4, which coincides with a period of decrease of pH from 8.2 to 5.4 (final pH of the solution was 8.9). In the case of $Cu_{0.75}Mg_{0.25}Al_2O_4$ similar trend is observed, as shown in Fig. 6. In presence of this catalyst at pH 8.4 and 10.7 a slight increase in TOC removal (67% and 71%, respectively) was observed after 4 h of reaction when compared to the reaction at lower pH 3.9 (63%).

It is interesting to note that the profiles shown in Figs. 5 and 6 for these two catalysts indicate that TOC removal decreases during the first 2 h, when a decrease in pH was observed, and then rises after increase in pH. As at this range, pH of solution is lower than pH_{PZC} of catalysts, the subsequent increase of pH may have been produced by the uptake of H^+ from water to produce $-M-OH_2^+$ on surface, as no buffer was used [30].

4. Conclusions

Clofibric acid can be effectively degraded by catalytic ozonation with HT-derived materials with improved stability and activity.

The highest activity and stability for CFA ozonation were observed over $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.5}Al_2O_4$, achieving mineralization degrees up to 58% and 55%, respectively, for 2 h reaction, and 71% and 79%, respectively, for 6 h reaction. Better performance was observed with HT and spinel type materials compared to impregnated catalysts, due to the better dispersion of the active phases in the support. Fe-HT was already stable after calcination at 900 °C and Cu-HT attained stability after calcination at 950 °C and pretreatment with oxalic acid. The stability of $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.5}Al_2O_4$ was confirmed after three consecutive runs. Also, XRD analysis of used catalysts showed similar crystallographic

structures that fresh material. The experiments proved that the efficiency of the process in the degradation of CFA is mainly attained by a heterogeneous, radical based mechanism. The efficiency of the process is not significantly affected by the initial pH of the solution.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2013.11.042.

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